

EFFECT OF BED MATERIALS MIXING ON THE OBSERVED BED SINTERING

Pavleta Knutsson^{1*}, Georg Schwebel¹, Britt-Marie Steenari¹, Henrik Leion¹

¹*Department of Environment and Inorganic Chemistry, Chalmers University of Technology, Gothenburg 41196, Sweden*

*Email: pavleta.knutsson@chalmers.se

ABSTRACT

The most widely used bed material in the existing fluidized bed systems is silica sand. Upon burning fuels with high alkali content, such as biomass, in a bed of silica sand, alkali silicates are formed as molten glassy phase that easily stick and form agglomerates, defluidization of the reactor and unplanned operational stops. Several materials have been tested as alternative bed materials, often containing aluminate minerals. Due to the relatively high cost of such bed materials the most dominant practice is still the use of silica sand even with high alkali fuels and the bed sintering is controlled by continuous replacement of the bed material.

The present study investigates the possibility of mixing bed materials and thereby optimizing the existing process by combining the low cost of silica sand with the sintering inhibiting properties of bauxite. Silica sand and bauxite were mixed in different ratios in a series of tests and were exposed to alkali compounds in a 12 MW boiler as well as in simplified experiments in a lab-scale furnace. The performance of the mixture of bed materials was then evaluated based on the tendency to chemically interact with the alkali compounds, the formation of agglomerates and the effect on the overall performance of the reactor. Thermodynamic predictions of the expected compounds at the given conditions were also used to compare with the experimentally obtained results.

It was observed that mixing bed materials led to change in the observed mechanism of agglomeration and is beneficial for the fluidization. Furthermore, when calcium was present the amount of the formed alkali silicates and thereby the amount of agglomerates was decreased. It could be therewith shown that a significant improvement can be reached with existing bed materials.

INTRODUCTION

In the recent years there has been an increasing interest globally in exchanging the existing fuels for heat and power generation with sustainable and CO₂-neutral alternatives such as waste or biofuels. Although providing a climate-smart alternative, the change to biogenous fuels and waste-derived fuels is a challenging step as it can cause severe operational problems. The main concern with the change of the fuel is the biomass ash. Biomass ashes contain high amount of alkali metals (mostly K, but also Na), alkali-earth (Ca and Mg) metals, Si, P and minor elements (Vassilev et al., 2013a; Vassilev et al., 2013b; Vassilev et al., 2013c). The low melting point of the ash and the ash-bed material interactions are widely described problems when fuels with high alkali content are used (Boström et al., 2009; Scala and Chirone, 2008; Skrifvars et al., 1994; Skrifvars et al., 1999; Steenari et al., 2009; Visser et al., 2008; Zevenhoven-Onderwater et al., 2000; Öhman et al., 2000). Upon release, the ash components interact with the bed material which results in sintering of the bed particles and eventually to bed failure and unplanned operational stops. Many investigations of the possible agglomeration mechanisms have been published (Brus et al., 2005; Ergudenler and Ghaly, 1993; Ghaly et al., 1994; Lin et al., 2003; Scala and Chirone, 2008). However, still problems with agglomerates and defluidization in FBC boilers make it necessary to further investigate the mechanism of bed sintering.

The most widely used bed material in the existing fluidized bed reactors is silica sand. When using fuel with high alkali content, which is the case of the majority of biogeneous fuels, with a bed material consisting of silica sand, alkali silicates are formed as molten glassy phase that easily stick and form agglomerates.

Different materials have been tested as alternative bed materials that could be used to avoid the formation of glassy matter inside the reactor (Almark and Hiltunen, 2005; Han et al., 2008; Shimizu et al., 2006). Due to the relative high cost of the tested bed materials the most dominant practice is still the use of silica sand even

with high alkali fuels where the bed sintering is controlled by continuous replacement of the bed particles (Almark and Hiltunen, 2005; Davidsson et al., 2008).

The present paper represents a new approach to solving the bed agglomeration problems. With the difference from previous studies where new bed materials or additives were tested, in the present paper a mixture of two already studied bed materials – silica sand and bauxite – is used. The study also uses a novel approach with the combination of exposures of the bed material in an industrial fluidized bed reactor as well as in controlled laboratory exposures. The goal was to optimize the existing process by combining the low cost and the availability of the silica sand with the known sintering inhibiting properties of the bauxite. The aim was not only to improve the observed agglomeration, but also to gain a better understanding on the bed-ash interaction.

EXPERIMENTAL

Initial experiments were carried out in a 12 MW CFB boiler that was built for research purposes. A schematic drawing as well as description of the boilers performance can be found in publications by Thunman et al. and Larsson et al (Larsson et al., 2013; Thunman et al., 2013). Wood pellets (0.45 wt% ash content, 0.04 wt% K content in pressed pellet) were used as fuel and bauxite (88.5% aluminium calculated as Al_2O_3) and a mixture of bauxite and silica sand as bed materials.

Further simplified experiments with the bed materials were performed in a horizontal furnace in laboratory conditions. For the lab experiments bauxite and silica sand were used as bed materials and K_2CO_3 and CaCO_3 as biomass ash components of major importance. The bed materials were fully mixed with the selected ash components to a constant mass ratio of 2:1 (bed material:ash component). The homogenized mixture was placed in an alumina crucible and heated in a horizontal tube furnace to the desired temperature at the rate of $10\text{ }^\circ\text{C}/\text{min}$ in air. The conditions were held for a period of 9 hours. The chosen temperature for the exposures was set to $800\text{ }^\circ\text{C}$. After completion of the tests, the materials were cooled to room temperature, weighed and further characterized as described below.

The crystal phase characterization of all the materials was performed by X-ray powder diffractometer (XRD, Siemens D5000 with CuK_α characteristic radiation). The chosen step size was 0.05° and the extracted profile was between 20 and $90^\circ 2\theta$.

For the morphological changes of the material and the characterization of the formed agglomerates as well as their chemical evaluation a Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS, Quanta 200FEG with an Oxford EDS system) was used. The microscope was run in high vacuum mode at an accelerating voltage of 15 kV. When cross-sections of the materials were of interest the materials were fixed in epoxy resin, sliced and polished. When artifacts due to charging were observed a gold coating was applied prior to analyses.

FactSage, version 6.3 was used for prediction of the phases that are thermodynamically stable under the present conditions. FactSage was run in its Equilib module and FTsalt, FToxid and FACT53 were used as databases (Bale et al., 2002).

RESULTS AND DISCUSSION

The unexposed materials were analysed using XRD and found to contain corundum Al_2O_3 in the case of calcined bauxite and α -quartz SiO_2 and minor amounts of aluminium silicate $\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_{2.25}$ in the case of silica sand.

Fig. 1 is a representation of the results obtained for bed material particles from the test with a bed material consisting of close to 50% silica sand and 50% bauxite in the 12 MW boiler. Limited amount of agglomerates were observed when bauxite was used as a bed material in the industrial scale reactor. Even though the morphology of the bed materials appeared as intact, still the chemical composition obtained by SEM-EDS showed the formation of an outer calcium layer around the particles which increased in thickness with the exposure time. When silica sand was added to the bed a Ca layer formed also around the sand particles and increased in thickness with exposure time. The formation of layered ash coating and an outer layer of Ca are in agreement with results published by other authors (Scala and Chirone, 2008; Visser et al., 2008; Vuthaluru and Zhang, 2001).

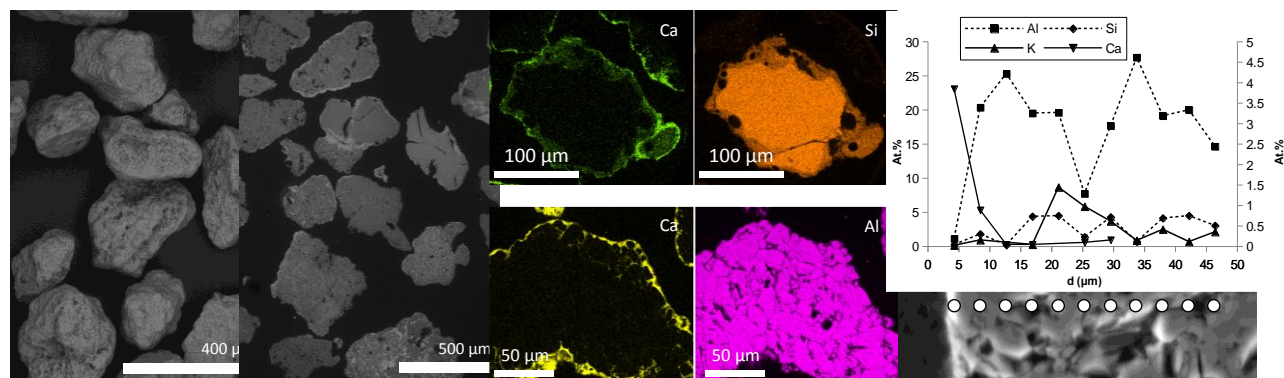


Fig. 1. SEM image of the bed particles after the exposure in the 12MW boiler. From left to right: top view of the collected particles, cross-section, Ca-layer formed on silica and bauxite particles, element profiles within a sampled bauxite particle (solid lines follow right axis, dashed – left one).

In the case of mixed bed material, when Ca layer was formed, a decrease in the same locations of K content was observed. It could be seen that with the increase of the measured calcium concentrations in the outer layer from 5 to 10 at.%, the concentration of potassium within the particle decreased from 1.5 wt.% to close to 0 wt%. This observation can be associated with a limited diffusion of the formed melt through the outer Ca-layer, but this process still needs further investigation. Typical element profiles obtained for the outer part of the ash layer are shown in Fig. 1. From the element profiles the formation of K, Ca Al, Si – rich compounds can be expected at the locations where a decrease in Si and Al concentrations can be connected to an increase in K and Ca.

Based on the observed elemental profiles further simplified tests were performed in a lab-scale furnace with only bauxite, sand, K_2CO_3 and $CaCO_3$. The exposed materials, the compounds identified by XRD, the degree of agglomeration and the stable phases calculated assuming thermodynamic equilibrium are summarized in Table 1. The thermodynamic calculations showed a good agreement with the results determined by XRD and with the element composition obtained by EDS.

Table 1. Summary of the new phases formed, the compounds theoretically predicted at 800 °C and an evaluation of the degree of agglomeration seen in the experiments

Bed material+ ash component	XRD	FactSage	Agglomeration degree
K_2CO_3 +silica sand	$KSiO_4$	$K_2Si_2O_5(s)$	strong
K_2CO_3 +bauxite	$KAlO_2$	$KAlO_2(s)$	weak
K_2CO_3 +silica sand+bauxite	$KAlSiO_4$	$KAlSiO_4(s)$, $KAlO_2(s)$	weak
$CaCO_3$ + silica sand	$CaCO_3$, SiO_2	Equilibrium composition not obtained	none
$CaCO_3$ +bauxite	$CaCO_3$, Al_2O_3 , $AlO(OH)$	$CaAl_2O_4$	none
$CaCO_3$ +silica sand+bauxite	$CaCO_3$, SiO_2 , Al_2O_3 , $AlO(OH)$	$CaAl_2Si_2O_8(s)$, $Ca_2Al_2SiO_7(s)$	none
$CaCO_3$ + K_2CO_3 +silica sand	$K_2Ca_6Si_4O_{15}$, $K_{4.8}Ca_{0.6}Si_6O_{15}$, $K_4CaSi_3O_9$, Ca_2SiO_4	K_2SiO_3 , $Ca_3Si_2O_7$	strong
$CaCO_3$ + K_2CO_3 +bauxite/	$KAlO_2$, $K_2Ca(CO_3)_2$	$KAlO_2(s)$, $CaAl_2O_4(s)$, $K_2Ca(CO_3)_2(s)$	none
$CaCO_3$ + K_2CO_3 +silica sand+bauxite	$K_4CaSi_3O_9$, $KAlO_2$, $CaAl_2Si_2O_8$	$KAlO_2(s)$, $KAlSiO_4(s)$, $Ca_3Si_2O_7(s)$	none

In the cases where the materials were exposed separately to K_2CO_3 (Fig. 2), as expected the most severe agglomeration was observed for the silica sand. In the case of K_2CO_3 -sand system, the formed ash melt was initially transported to locations rich in Si where silicates were formed as a sticky glue-like layer throughout the bed particles that allowed for the agglomerate to grow further in all directions and resulted in dense uniform structure agglomerate. The formed glassy phase was identified as $KSiO_4$. $K_2Si_2O_5$ was the phase expected from thermodynamic equilibrium calculations.

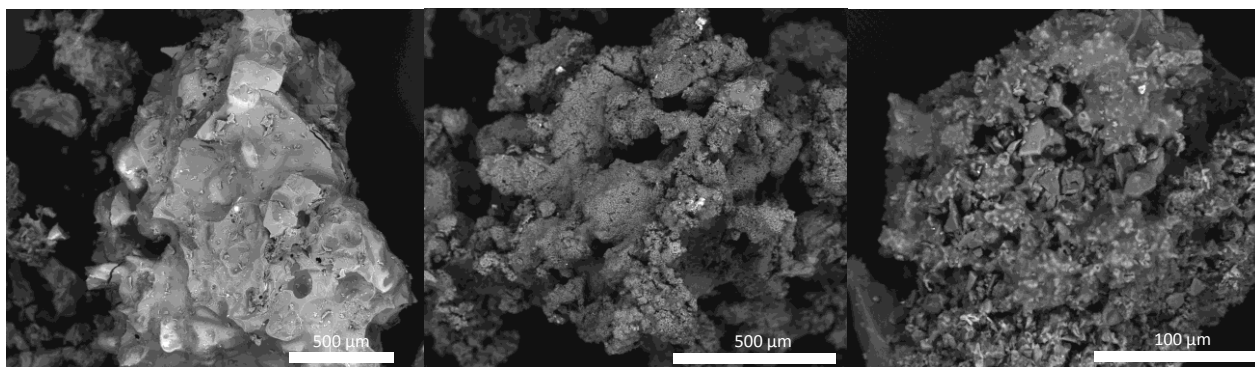


Fig. 2. SEM top-view images of the typical agglomerates formed in the cases of (from left to right): K_2CO_3 and sand, K_2CO_3 and bauxite, K_2CO_3 and mixture of sand and bauxite

For bauxite - $KAlO_2$ was expected both by theoretical calculations and identified after exposure and weaker agglomeration could be observed. The agglomerate appeared porous but still similar in size to the one formed in the case of silica sand.

Mixing of the bed materials led to a weaker agglomeration and the formation of mixed aluminium silicates – $KAlSiO_4$ together with small amounts of $KAlO_2$. When bauxite is added the degree of agglomeration is decreased mainly due to the dilution effect as the addition of bauxite decreases the amount of silica available for the formation of low melting silicates. At the same time the formed $KAlO_2$ did not have the glue-like effect that led otherwise to agglomeration. According to FactSage calculations, these were the phases also expected when equilibrium is reached. K showed a clear preference for sites rich in Si. No locations where a pure $KAlO_2$ (with no dissolved Si) occurred could be identified from the EDX analysis of cross-sections of the particles, where instead a $KAlSiO_4$ or $KSiO_4$ could be assigned to the concentration profiles. The experimental set-up where both bed materials were used can also be compared with previous results obtained when kaolin was used as an alkali capturing additive within the bed (Davidsson et al., 2008; Steenari and Lindqvist, 1998) .

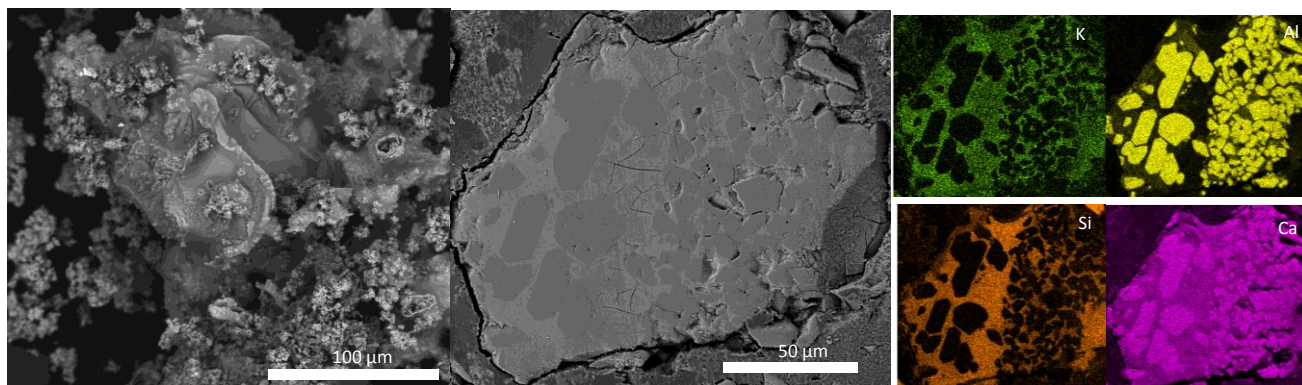


Fig. 3. SEM image (left) and EDS elemental maps (right) of a cross-section showing the agglomerate formed in the case of mixture of $CaCO_3$, K_2CO_3 and silica sand and bauxite.

$CaCO_3$ caused a significant decrease of the degree of the agglomeration during all the exposures except for the one with pure silica sand. This effect was previously shown by other authors when studying the effect of the use of additives for counteracting agglomeration (Vuthaluru and Zhang, 2001). Porous agglomerate and mixed silicates and aluminates were formed (elemental maps, Fig. 3), even though only Ca-silicates were predicted to be thermodynamically stable by FactSage at the conditions of the exposures. From the intensity-based elemental maps the effect of the Ca could be observed. Lower concentrations of K were measured at locations rich in Si if compared with the K_2CO_3 - SiO_2 case. The structure of the formed agglomerate with lower K concentrations showed also that a thin outer Ca-rich layer was formed similar to the one obtained at the samples exposed to the industrial scale reactor. Mixed silicates were detected by XRD – $K_4CaSi_3O_9$ and $CaAl_2Si_2O_8$ but these were difficult to quantify and localize from the EDS point analyses.

Two major mechanisms are described in the literature as responsible for the agglomerate formation (Brus et al., 2005; Grimm et al., 2012; Piotrowska et al., 2012; Öhman et al., 2005) : 1) by melting and gluing; e.g. in the case where silica is present, the agglomerates are considered to form as a result of the initial formation of

alkali silicates that have a low-melting point and act as a glue, causing the particles to stick to each other; 2) by diffusion and dissolution of formed compounds in the formed ash melt; e.g. in the case where calcium is present the mixed silicates are considered to form as a result of the formation of reaction product that causes the particle to attach to each other.

In the present case where both Si and Ca were present in the experimental set-up, the lack of a formed melt and the formation of a Ca-layer that led to a decrease in the measured K concentrations, are suggesting a mechanism where Ca inhibits the diffusion and dissolution of agglomeration inducing elements, most importantly K. Thus, the second mechanism is the dominating one.

When a mixture of K_2CO_3 and $CaCO_3$ is present, a Ca-rich layer is formed around the particles and acts as a barrier that hinders further transport of the K-rich melt into the particle. This limits its access to the SiO_2 -rich areas and slows down the formation of the glue-like compound that leads to a build-up of agglomerates. As a result the few formed agglomerates are more brittle and smaller in size.

CONCLUSIONS

Mixtures of two minerals that have been extensively studied as single bed materials in FBC – silica sand and bauxite were tested in an industrial-scale boiler as well as in simplified lab furnace exposures. The exposed materials were characterized in terms of the degree of agglomeration that occurred. Through material characterization using XRD, SEM-EDS and based on theoretical calculations using FactSage the ash-bed materials interactions were followed which resulted in an elaboration of a dominating mechanism. The following conclusions could be drawn:

- K is detrimental for agglomeration. The agglomeration was weaker in the case where bauxite was used as bed material than when silica was used as the single bed material
- Using a mixture of silica and bauxite as bed material did not stop the agglomeration but decreased its extent
- Ca did not cause agglomeration with any of the tested bed materials
- When Ca is present, a Ca-rich layer is formed around the particles that acts as a barrier for the diffusion of the low-melting K-rich melt
- When both Ca and Si are present the dominating mechanism for the formation of agglomerates seems to be through dissolution of Ca in silicate melt and limited diffusion of K as a result of the formation of Ca-layer
- FactSage and SEM-EDS results showed a good agreement with the results obtained by XRD in laboratory experiments
- The laboratory experiments were shown to reflect the processes observed in the industrial scale boiler fairly well and therefore can be further used for prediction of bed-ash interactions.

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